while the vapor-enriched solution (S)2 carried off at
the bottom of the second phase separator (53) is conveyed
by the solution pump (54) through the solution heater (51)
and introduced at the head into gas vapor enricher (52)
that is combined with the first phase separator and the
vapor-depleted solution (S)1 carried off at the bottom of
the gas vapor enricher (52) is fed again to the liquid
channel of the reaction cell (50).

REMARKS

All previous advisory actions, have been carefully
reviewed and considered. Claims have been carefully
reviewed to conform to the requirements and to office
action dated 6/29/2001. Reconsideration and allowance are
respectfully urged.

Please note that claims mentioned in the new
specifications are numbered from 1 to 15, referring to the
15 newly entered claims numbered 30 - 44 in the claim set
that will be renumbered after allowance. Therefore,
claim 1 in the specifications refers to claim 30 (new),
claim 2 in the specifications refers to claim 31 (new),
claim 3 in the specifications refers to claim 32 (new),

claim 4 in the specifications refers to claim 33 (new),

claim 5 in the specifications refers to claim 34 (new),

claim 6 in the specifications refers to claim 35 (new),

claim 7 in the specifications refers to claim 36 (new),

claim 8 in the specifications refers to claim 37 (new),

claim 9 in the specifications refers to claim 38 (new),

claim 10 in the specifications refers to claim 39 (new),

claim 11 in the specifications refers to claim 40 (new),

claim 12 in the specifications refers to claim 41 (new),

claim 13 in the specifications refers to claim 42 (new),

claim 14 in the specifications refers to claim 43 (new),

claim 15 in the specifications refers to claim 44 (new).

All issues found in the new claim set have been introduced in the original claim set. No new issues are introduced. The term "negligible current flow" was introduced on page 2/16 of the specifications in the original application; the term "media conveying devices" was introduced in original claim 5.

New claim 30 is corresponding to original claim 1 in which the term "reduced quantity" was introduced for the stoichiometrically consumption of gas and vapor. To overcome the infinite scope of the term "reduced quantity" the term "stoichiometric reduced quantity" found in the

original specification is now used in the claim to be more

specific. The term "short-circuited" was changed to the

suggested term "connected". The term "adapted vapor partial

pressure", the cause of the adaptation and its source are

explained in Fig. 3. In combination with Fig. 4 all

materials undergoing the electrochemical reaction are cited

and explained. The term "stoichiometric" specifies the term

"consumption" and the term "liberation" was changed to

"recovery" to clearly point out the nature of the

electrochemical reaction without any losses of substance.

Claim 31 is corresponding to original claim 2 in the

original claim set where the term "migrate transversely

through the solution" can be found. The term "short-

circuited" was changed to the suggested term "connected".

The term "adapted vapor partial pressure" was changed to

"same medium" vapor partial pressure, the amount and its

source being explained in Fig. 3. In combination with Fig.

4 all materials undergoing the electrochemical reaction are

cited. The term "stoichiometric consumption of gas and

vapor by generating ions" specifies the term "consumption";

the term "liberation" was changed to "recovery", pointing

out that nothing is lost in the circuit system. The term "

stoichiometrically reduced quantity" specifies the amounts

of gas, vapor and solution participating in the

electrochemical reaction.

Claim 32 is corresponding to original claim 5 in

connection with claim 1 in the original claim set. The term

"substance phase quantities" are now explained by quoting

the descriptive figures and phases. The "media-conveying

devices" introduced in the specifications of the original

claim set are named in the new claim. In combination with

figures 3 through figure 6 the terms "substance phase

quantities" and "ternary substance circulation" have now

clear antecedents.

Claim 33 is corresponding to original claim 4 in

connection with original claim 1.

Claim 34 is corresponding to original claim 3 in

connection with original claim 1.

Claim 35 is corresponding to original claim 6 in

connection with original claim 1.

Claim 36 is corresponding to original claim 7 in

connection with original claim 5. The term „substance phase

quantities" are now explained by quoting phases and descriptive figures 3 and 4.

Claim 37 is corresponding to original claim 8 in connection with original claim 6.

Claim 38 is corresponding to original claim 5 in connection with original claim 2. The term "substance phase quantities" are now explained by quoting the descriptive Figures and phases. The "ternary substance circulation" is described in Fig.3 and Fig. 5.

Claim 39 is corresponding to original claim 4 in connection with original claim 2.

Claim 40 is corresponding to original claim 3 in connection with original claim 2.

Claim 41 resembles part of original claim 3 in connection with original claim 2.

Claim 42 resembles original claim 6 in connection with original claim 2.

Claim 43 resembles original claim 7 in connection with original claim 2.

Claim 44 resembles original claim 8 in connection with original claim 2. The term „substance phase quantities" are now explained by quoting phases and descriptive figures 3 and 4.

In Figure 7, an obvious mistake was corrected. When connecting two or more electrical resistors parallel, Ohm's law allows adding the current flows, but not the voltage differences. Therefore, when the parallel-connected electrostatic voltage source is turned on, the actual working voltage of the system can only change from the inherent voltage difference of the reaction cell to the electrostatic voltage difference ($\Delta Ueff. = \Delta Uest.-(Iz-1/2I_D)x Rz$). This obvious mistake was also corrected in the original specifications on page 2/16.

Figures 1 through 7 are newly submitted to correct this, as well as typographical errors in the numbers. The substance flow quantities in Fig.4 and Fig.6 were numbered according to the individual state point numbers used in Fig.3 and Fig.5 to define the components undergoing the

electrochemical reaction and their state at specific points throughout the circular process.

Please note that the address for correspondence has been changed and a revocation of power of attorney is on file.

In view of the above, it is respectfully submitted that the claims are now in condition for allowance, and favorable action thereon is earnestly solicited.

Respectfully submitted,

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Galvanosorptive reaction cell

The invention relates to a galvanosorptive reaction cell for ~~the~~ conver~~sion~~ting ~~of~~ sorptive reaction work into useful electrical work by means of a galvanic reaction cell comprising feeding to and carried off~~, whereby~~ a ternary substance system consisting of a carrier gas ∕ vapour mixture and a solution absorbing the vapour component in the cell housing, ~~is fed to and carried off from the reaction cell,~~ as well as the formation of the fed-in and carried-off substance flows into an isobaric substance circuit with thermal decomposition of the solution and separation of the solution components outside the reaction cell.

A galvanic reaction cell of a modified type, with hydrogen and an aqueous ammonia solution in an isobaric substance circuit with thermal decomposition of the solution and re-liquefaction of the evaporated solution component carried out outside the reaction cell is known from DE 3302635 A1. However, ~~Both~~ the design of the galvanic reaction cell and the design of the isobaric substance circuit as described in DE 3302535 A1 are disadvantageous for the galvanic reaction mechanism inside the cell and its operational behaviour.

~~On the one hand,~~ ~~t~~The ammonia being fed in liquefied form on the cathode side to the reaction cell contains residual portions of water, which during the operation is lead~~s~~ing to a constant dilution of the liquid ammonia in the reaction cell and thus after a short time to an operational standstill, because a continuous extraction of diluted ammonia from the cell is lacking. ~~On the other hand,~~ In addition the non-meterable substance circuit gives rise to an unsteady power and voltage behaviour of the reaction cell. Moreover, the method, in which the waste heat of the ammonia liquefaction is to be left in the substance circuit and the thermal efficiency of the ~~thermo~~

galvanic energy conversion thereby raised, is based on process features that do not permit a recovery of the liquefaction waste heat, for example the liquefaction of overheated ammonia vapour at a higher temperature than the saturation temperature.

In addition, on account of the low solubility of gaseous hydrogen in liquid ammonia the stoichiometric introduction of the reactants to the reaction zone of the cathode is possible only to a limited extend, which has a diminishing effect on the substance conversion and thus on the electrical energy yield. An additional reduction of the energy yield arises due to the partial vapour pressure drop resulting from the isobaric mixing of hydrogen and liquid ammonia inside the reaction cell.

A ~~n in principle~~ different kind of reaction cell with a closed isobaric substance circulation is known from the documents DE-OS 1596143 and DE-OS 1599153. An aqueous hydrogen halide solution acts as the substance system, said hydrogen halide solution being partially decomposed electrolytically, i.e. ~~with the~~ by adding ~~tional of~~ electrical energy it decomposes ~~in~~ to elementary hydrogen and the corresponding liquid halogen, whereby the decomposition products are fed again ~~fed~~ to a recombination cell and converted into the aqueous initial solution with the release of electrical energy. Here, a finite amount of ambient heat is to be converted into useful electrical energy, which former ultimately results from the useful voltage difference of both process steps. Use is made inside the recombination cell of the chemical reaction work and not the sorptive reaction work, which is lost with the disclosed recombination cell and therefore can be expended as additional electrical energy in the electrolytic separation.

The basis adopted here was the ideal voltage values of the decomposition and the recombination of the substance system,

which are known to represent equilibrium values and consequently do not show any substance conversion into one of the reaction directions. As soon as a noticeable substance conversion is generated, the voltage values of both reaction steps become alike, as a result of which the disclosed work gain is reduced. In addition, the loss of the sorptive reaction work reduces the work gain, so that a technical exploitation of this effect holds out little promise.

Furthermore, there is described in EP 0531293 an isobaric process for the conversion of sorptive reaction work into electrical work with a closed ternary substance circulation with the use of a carrier gas and a thermally decomposable, sorptively acting aqueous solution, whereby the energy conversion is intended to be carried out in a galvanosorptive reaction cell, the thermal decomposition of the solution and separation of the solution components on the other hand outside the reaction cell. Further galvanosorptive and electrochemical energy conversion processes with isobaric substance circuits are known from EP-OS 91917497. Neither the design of this novel, galvanosorptive reaction cell, nor the reaction mechanisms taking place inside the reaction cell and influencing the design emerge from these two documents, so that an essential prerequisite for the technical exploitation of the principle is lacking.

Therefore, ~~a~~ one ~~task~~ goal of the invention ~~therefore~~ is the design ~~in principle~~ of a technically exploitable, galvanosorptive reaction cell for the conversion of sorptive reaction work into useful electrical work by taking account of the reaction mechanisms taking place inside the cell in the sorption process. Another ~~task~~ goal of the invention is the formation of the fed-in and carried-off substance flows into an operationally stable, regulatable, isobaric substance circuit

with high process efficiency, whilst avoiding the previously mentioned disadvantages of the galvanic reaction cell. A ~~f~~Furthermore, ~~task of~~ the invention ~~is the~~ aims to increase ~~of~~ the electrical energy yield of this galvanosorptive reaction cell over and above the substance conversion by utilising the latent and sensitive heats contained in the substance flows fed to it.

The ~~task of the~~ goal to develop a technically exploitable design ~~in principle~~ of a galvanosorptive reaction cell is reached by combining the ~~solved with the combinations of~~ features of claim 1 for a membrane electrolyte cell or by combining ~~and with~~ the ~~combinations of~~ features of claim 2 for a liquid gap cell, whereby both cell configurations ~~enable~~, without geometric modifications, ~~both~~ enable the anion-generating and the cation-generating reaction mechanism. With the sorptive liquefaction of the vapour in the solution generating useful electrical work, premature substance conversion limitations of the galvanic reaction cell are removed in an advantageous way for the galvanosorptive cell, ~~as~~ for example, the low hydrogen solubility in liquids and the inability of the galvanic cell ~~to~~ gain a portion of the liquefaction heat directly as reaction work. Therefore, ~~In this way~~ galvanosorptive reaction cells achieve higher energy yields and efficiencies than galvanic reaction cells.

As described in claim 5 and claim 11 ~~According to the combinations of features of claim 3,~~ any sorptive liquid mixtures thermally decomposable into a vapour component and an absorbing liquid component~~,~~ can be used in combination with a carrier gas forming ions with the vapor component, i.e. ~~as for example~~ hydrogen or oxygen, in order to start the galvanosorptive reaction process ~~can be used~~ in the

galvanosorptive reaction cell.~~s for the galvanosorptive reaction process.~~

As described in claim 12 ~~A~~an electrolyte soluble in the solvent ~~and~~ with an, in comparison to the partial pressure of the vapor component insignificant ~~negligible~~ inherent vapour pressure can be added to the individual substance system ~~if need be~~ in order to improve the ion conductivity~~,~~ and likewise ~~as a result of which~~ the internal resistance of the reaction cell can be reduced in an advantageous manner. The structural materials of these reaction cells do however need to be suited to the selected substance system.

Such sorptive liquid mixtures combinable with a carrier gas are for example the aqueous solutions of NH_3, H_2SO_4 or $LiBr$ or the solution $NH_3/LiNO_3$. These and further solutions were investigated by Niebergall in "Working substance pairs for absorption refrigeration systems" ~~with~~ in regard to their utilis~~abili~~ty at low temperatures. The low-temperature use of these solutions is also advantageous for the thermo-galvanic energy conversion, because the waste heat of many technical processes can ~~thus~~ be used as a cost-free, convertible heating energy potential.

According to the process features described in claim 3 or claim 9 ~~of claim 5,~~ the vapour partial pressure difference acting in the galvanosorptive cell between the carrier gas-vapour mixture and the sorptive solution can be raised not only~~,~~ by adjusting ~~via~~ the overall system pressure P_{total} and hence ~~via the one-off~~ by carrier gas filling, but also ~~via~~ by conveying the circulation rate of the vapour-storing carrier gas ~~conveyed~~ in the circuit. This gives rise to an increase in the useful voltage without additional mechanical loading of the built-in cell components, with only slightly higher power consumption of

the gas compressor arranged in the external part of the substance circuit. This advantageous possibility is likewise not available with the galvanic reaction cell disclosed in DE 3302635 A1.

The adiabatic running of the process inside the galvanosorptive reaction cell leads to ~~results in~~ a simplified cell ~~design in terms of its structure~~, because it is possible to dispense ~~with corresponding~~ heat transfer channels inside the cell. According to the features ~~of~~ in claim 4 or claim 10~~,~~ such channels are required for the non-adiabatic running of the process. ~~Through them flows a~~ A heat transfer medium for cooling or heating the reaction cell is flowing through these channels. ~~p~~Preferably a solution of the same kind~~, which is~~ as in the reaction process can be used, which is only in thermal contact with the absorbing solution and the electrode wetted by the solution. ~~and can both cool and heat the reaction cell~~.

The ~~task~~ goal of increasing the electrical energy yield of the galvanosorptive reaction cell is accomplished as described in ~~solved according to~~ claim 6 or claim 13 with the assignment of an activation source, which permanently confers ~~on the electrodes~~ a ~~quasi~~ electrostatic voltage difference to the electrodes from the outside with a very low electric current flow, whereby the latter can amount to several volts and is superimposed on the inherent voltage difference of the cell. It gives rise within the reaction cell to a sorptive vapo~~u~~r liquefaction along with a temperature drop of the concentrating solution, whereby the applied voltage difference is proportional to the temperature drop and inversely proportional to the increase in vapor component concentration of the solution and is available as a working voltage difference at the external load resistor less the cell voltage losses. Using this measure, the power density of the galvanosorptive cell is ~~also~~ increasing~~ed~~

apart from the useful electrical work yield and the thermal efficiency ~~further~~ is raising~~ed~~.

With the combinations of features of claim 7 or claim 14, the substance flows fed to and carried off from the reaction cell are formed into an isobaric, substance circuit, which makes the substance potential difference of the galvanosorptive reaction cell available in an operationally stable fashion ~~the substance potential difference of the galvanosorptive reaction cell~~, and therefore can be ~~is~~ regulated~~able~~ via the flow rates of the conveying devices independent of one another (solution pump and gas compressor) and exhibits a high thermo-galvanic efficiency with the combined process components.

If the electrostatic voltage of the activation source acts on the reaction process inside the galvanosorptive reaction cell, then with the combinations of features of claim 8 or claim 15 the process engineering expenditure in the external part of the substance circuit is clearly simplified and the energy yield of the galvanosorptive reaction cell increased.

The invention is described with the aid of the figures 1 to 7. In detail, the figures show:

Fig. 1: ~~t~~The functional principle and the schematic structure of a universally utilisable, galvanosorptive membrane electrolyte cell, with the exemplified representation of a cation-generating, ternary substance system ~~SII~~ SI: $[H_2^g, NH_3^v]$ $[\text{\sout{$H_3O$}}NH_4^{+EL}, El]$ $[NH_3^{aq}, H_2^g]$, and an anion-generating, ternary substance system ~~SI~~ SII: $[O_2^g, H_2O^v]$ $[OH^{-EL}, El]$ $[LiBr^{aq}, O_2^g]$,

Fig. 2: ~~t~~The functional principle and the schematic structure of a universally utilisable galvanosorptive liquid gap cell with the ex~~a~~emplified representation of a cation-

generating, ternary substance system ~~SIV~~ SIII: $[H_2^g, \; H_2O^v]$ $[H_3O^{+aq}, \; H_2SO_4^{aq}]$ $[H_2SO_4^{aq}, \; H_2^g]$, and an anion- generating, ternary substance system ~~SIII~~ SIV: $[O_2^g, \; H_2O^v]$ $[OH^{-aq}, H_2SO_4^{aq}]$ $[O_2^g, \; H_2SO_4^{aq}]$ and

Fig. 3:   ~~t~~The cyclic process and the substance states of an adiabatic galvanosorptive reaction cell in a schematic T/ξ and P/ξ diagram for an arbitrary, ion-generating, ternary substance system,

Fig. 4:   ~~t~~The functional circuit diagram of a galvanosorptive reaction cell with closed, isobaric substance circuit according to the cyclic process as per Fig. 3,

Fig. 5:   ~~t~~The cyclic process and the substance states of the galvanosorptive reaction cell with electrostatic support for an arbitrary, ion-generating, ternary substance system in a schematic T/ξ and P/ξ diagram,

Fig. 6:   ~~t~~The functional circuit diagram of a galvanosorptive reaction cell with electrostatic support and closed, isobaric substance circuit in accordance with the cyclic process as per Fig. 5, and

Fig. 7:   ~~s~~Schematically, the electrical equivalent circuit diagram of the galvanosorptive reaction cell with assigned activation source.

The structure and mode of functioning of the galvanosorptive membrane electrolyte cell will be explained in greater detail with the aid of the examples of embodiment of Fig. 1.

The membrane electrolyte cell consists of a cell housing (2), which is divided by a media - sealing, ~~galvanically separating~~ electrical isolating peripheral seal (3) into a first housing

part (2.1) and a second housing part (2.2). The housing (2) contains a flat-shaped, porous, gas-permeable first electrode (4) and a flat-shaped, porous, gas- and liquid-permeable, second electrode (5). Between the electrodes faces (4.2,5.2) either ~~there is arranged alternatively~~ a selectively cation- or a selectively anion-permeable membrane electrolyte (6) is arranged, which forms a mechanically stable composite unit with the porous electrodes (4,5). The first electrode face (4.21) facing away from the membrane electrolyte (6) forms ~~with the first housing part (2.1)~~ a slit-shaped gas channel (7) with the first housing part (2.1), through which ~~there flows~~ a vapour-saturated, cation-generating carrier gas type [G,V] or a vapour-saturated, anion-generating carrier gas type [G,V] is flowing. The second electrode face (5.21) facing away from the membrane electrolyte (6) forms ~~with the second housing part (2.2)~~ a slit-shaped liquid channel (8) with the second housing part (2.2), through which ~~there flows~~ an undersaturated, vapour-absorbing solution [S] is flowing. The electrodes (4,5) are ~~electrically short-circuited~~ connected with current lead-in and lead-off devices (9,10) and an external load resistor (11). The current lead-in and lead-off devices (9,10) represented schematically are arranged in Fig. 1 rotated through 90°. They are constructed geometrically like the conduction systems known from fuel cells, so that they only slightly reduce ~~only slightly~~ the reactive surfaces of the electrodes and do not hinder the through-flow of the slit-shaped channels (7,8).

As described in Fig.3 and Fig.4 ~~Via openings (12.1, 12.2) in the first housing part (2.1),~~ a vapour-enriched ~~saturated~~ carrier gas [G,V]~~4r~~, (ZP4) with high vapour partial pressure (P$_T$,Pv4) is fed via an inlet opening (12.1) in ~~to~~ the gas channel (7) and a stoichiometric reduced quantity of vapour-depleted ~~saturated~~ carrier gas [G,V]~~m~~, (ZP1) with reduced vapour partial pressure

(P_T, P_{v1}) is carried off via an outlet opening (12.2). Via an inlet openings (13.1, ~~13.2~~) in the second housing part (2.2), an undersaturated solution [S]$_2$~~p~~, (ZP2) with low~~er~~ vapo~~u~~r component concentration (ξ_{s2}) and low vapo~~u~~r partial pressure (P_T, P_{v2}) is fed to the liquid channel (8) and a two-phase mixture ~~[S]r, [G,V]p,~~ [S,G,V]$_3$, (ZP3) of undersaturated enriched solution [S]$_3$~~r~~, (ZP3) with high ~~raised~~ vapo~~u~~r component concentration (ξ_{s3}) and ~~low~~ medium vapo~~u~~r partial pressure (P_T, P_{v3}) and a recovered, moderately vapo~~u~~r-enriched ~~saturated~~ carrier gas [G,V]~~p~~$_3$ ~~, (ZP3)~~ in the solution with the same ~~low~~ medium vapo~~u~~r partial pressure (P_T, P_{v3}) is carried off via an outlet opening (13.2).

When ~~use is made of~~ a cation-generating gas type is being used, as for example hydrogen, and a membrane electrolyte (6) selectively letting through this cation type, cations are formed at the phase boundary (4.~~1~~2) (gas/solid/electrolyte) of the first electrode (4) as a result of anodic oxidation with the stoichiometric consumption of hydrogen and vapo~~u~~r from the gas channel (7). These cations migrate through the membrane electrolyte (6) to the second electrode (5) and at its phase boundary (5.1~~2~~) (gas/liquid/solid) increases the concentration of the absorbing solution flowing in the liquid channel (8) as a result of cathodic reduction, with the ~~liberation~~ recovery of an equivalent stoichiometric quantity of hydrogen in the solution. The electrons flow here from the first electrode (4) via the conduction devices (9,10) and the external load res~~i~~stor (11) to the second electrode (5).

When ~~use is made of a~~ an anion-generating gas type is being used, as for example oxygen, and a membrane electrolyte (6) selectively letting through this anion type, anions are formed at the phase boundary (4.2~~1~~) (gas/solid/electrolyte) of the

first electrode (4) as a result of cathodic reduction with the stoichiometric consumption of oxygen and vapour from the gas channel (7). These anions migrate through the membrane electrolyte (6) to the second electrode (5) and at its phase boundary (5.12) (gas/liquid/solid) increases the concentration of the solution flowing in the liquid channel (8) as a result of anodic oxidation with the ~~liberation~~ recovery of an equivalent stoichiometric quantity of oxygen in the solution. The electrons flow here from the second electrode (5) via the current conduction devices (10,9) and the external load resistor (11) to the first electrode (4).

Circled state points (ZP1 to ZP4), ~~To the fluid flows fed to and carried off from the membrane electrolyte cell according to Fig. 1 there are assigned the state points (ZP1 to ZP4) marked by circles,~~ which represent saturation equilibriums for the respective fluid flows, and their definition ~~are defined~~ by ~~their~~ state magnitudes [P,T,ξS,ξV] are assigned to the fluid flows fed to and carried off from the membrane electrolyte cell according to Fig. 1. They relate to the cyclic process according to Fig. 3. The substance potential difference of the galvanosorptive reaction process inside the membrane electrolyte cell arises with the local assignment of the substance flows on the reaction cell. Therefore ~~For this~~, the vapour-saturated gas flow is conveyed, with transverse consumption of a stoichiometric quantity of carrier gas and vapor. This is done ~~removal by suction of a partial quantity,~~ preferably in the opposite direction to the solution flow, but parallel to the electrode faces through the cell. ~~The vapour concentration ξV is constant during the reaction process.~~

An aqueous solution of lithium bromide in combination with oxygen as an anion-generating reaction system (SII) and an

aqueous ammonia solution in combination with hydrogen as a cation-generating reaction system (SI~~I~~) were selected as examples of ternary substance systems for the membrane electrolyte cell. Two ~~further,~~ other ternary substance systems of aqueous sulphuric acid in combination with oxygen (SI~~II~~V) and in combination with hydrogen (SIII~~V~~) are presented in Fig. 2 for the liquid gap cell. In the substance systems (SII, SIII and SIV), water is the vaporising mixture component and in substance system (SII) ammonia. The selected examples of ternary substance systems can be applied to both types of cell structure. The galvanosorptive reaction systems read as follows:

SI~~I~~: $[H_2^g, NH_3^v]$, $[NH_4^{+EL}, El]$, $[NH_3^{aq}, H_2^g]$ (cation-generating)

SII: $[O_2^g, H_2O^v]$, $[OH^{-EL}, El]$, $[LiBr^{aq}, O_2^g]$ (anion-generating)

SIII~~V~~: $[H_2^g, H_2O^v],]$, $[H_3O^{+aq}, H_2SO_4^{aq}]$, $[H_2SO_4^{aq}, H_2^g]$ (cation-generating)

SI~~II~~V: $[O_2^g, H_2O^v]$, $[OH^{-aq}, H_2SO_4^{aq}]$, $[H_2SO_4^{aq}, O_2^g]$ (anion-generating)

The electrode pairs and the membrane electrolytes [El] are indeed geometrically alike in the selected reaction systems, but differ in their mode of functioning and in the material structure. The electrode reactions are stated in greater detail for the substance system (SI~~I~~):

Reaction system(SI~~I~~): ~~a~~ $\alpha|$ $(NH_3^v, H_2^g)^{\alpha a}$ | NH_4^{+EL}, El | $NH_3^{aq}, H_2^g)^\beta$ | β

Cathode reaction ~~a~~α: $e^{a\alpha} + NH_4^{+EL} = (NH_3^v + \frac{1}{2}H_2^g)^{a\alpha}$

Anode reaction β: $(NH_3^{aq} + \frac{1}{2}H_2^g)^\beta = NH_4^{+EL} + e^\beta$

Cell reaction (~~a~~α+β): $e^{a\alpha} + (NH_3^{aq} + \frac{1}{2}H_2^g)^\beta = (NH_3^v + \frac{1}{2}H_2^g)^{a\alpha} + e^\beta$ Substance potential

difference: $(\varphi^\beta - \varphi^\alpha)_{st.} = (R \times T/F) \times \ln[(P_a/P_\beta)_{NH3aq} \times (P_a/P_\beta)^{\frac{1}{2}}_{H2}]$

Electrostatic potential

difference: $(\varphi^\beta - \varphi^\alpha)_{est.} = [Cp \times (T_1 - T_2)_{NH3aq.} \pm Q_{rev.}]/F$

As a further development of the invention, the structure and mode of functioning of a galvanosorptive liquid gap cell are described in greater detail with the aid of the examples of embodiment of Fig. 2.

The liquid gap cell consists of a cell housing (21), which is divided by a media sealing, ~~galvanically separating~~ electrically isolating peripheral seal (22) into a first housing part (21.1) and a second housing part (21.2). The housing (21) contains a flat-shaped, mechanically stable, porous, gas-permeable first electrode (23) and a flat-shaped second electrode (24) lying adjacent, without a gap, to the second housing part (21.2). The face of the first housing part (21.1) and the face (23.2) of the first electrode (23) facing one another form a slit-shaped gas channel (25), through which ~~there flows~~ a vapour-saturated, cation-generating carrier gas type [G,V] or a vapour-saturated, anion-generating carrier gas type [G,V] is flowing. The electrode faces (23.1, 24.1) facing one another form a slit-shaped liquid channel (26), through which ~~there flows~~ an undersaturated, vapour-absorbing, ion-conducting solution [S] is flowing. The electrodes (23,24) are electrically ~~short-circuited~~ connected with the current lead-in and lead-off systems (27,28) and an external load resistor (29). The gas-side current conduction system (27) is constructed geometrically like that of the gas electrodes of fuel cells and is represented schematically in Fig. 2 rotated through 90°.

As described in Fig. 3 and Fig. 4 ~~Via openings (30.1, 30.2) in the first housing part (21.1),~~ a vapour-saturated carrier gas [G,V]$_4$~~r~~, (ZP4) with high vapour partial pressure (P$_T$,P$_{V4}$) is fed to the gas channel (25) via an inlet opening (30.1) in the first housing part (21.1) and a stoichiometrically reduced quantity of vapour-depleted ~~saturated~~ carrier gas [G,V]$_1$~~m~~, (ZP1) with a reduced vapour partial pressure (P$_T$,P$_{V1}$) is carried off via the

outlet opening (30.2). ~~Via openings (31.1, 31.2) in the second housing part (21.2),~~ aAn undersaturated, depleted solution $[S]_{2P}$, (ZP2) with ~~reduced~~ low vapour component concentration (ξ_{S2}) and low vapour partial pressure (P_T, P_{V2}) is fed to the liquid channel (26) via an inlet opening (31.1) in the second housing part (21.2), and a two-phase mixture ~~[S]r, [G,V]p,~~ $[S,G,V]_3$, (ZP3) of undersaturated enriched solution $[S]_{3T}$, (ZP3) with ~~raised~~ high vapour component concentration (ξ_{S3}) and ~~low~~ medium vapour partial pressure (P_T, P_{V3}) and a recovered vapour-enriched ~~saturated~~ carrier gas $[G,V]_{3P}$, in the solution ~~(ZP3)~~ with the same ~~low~~ medium vapour partial pressure (P_T, P_{V3}) is carried off via an outlet opening (31.2)

When ~~use is made of~~ a cation-generating gas type, ~~such as~~ i.e. hydrogen, is used, cations are formed at the phase boundary (23.1) (gas/liquid/solid) of the first electrode (23) as a result of anodic oxidation with the stoichiometric consumption of hydrogen and vapour from the gas channel (25). These cations migrate transversely ~~to~~ through the solution flowing ~~through~~ in the ion-conducting liquid gap (32) to the second electrode (24) and at its phase boundary (24.1) (gas/liquid/solid) increases the concentration of the solution flowing in the liquid channel (26) as a result of cathodic reduction with the ~~liberation~~ recovery of an equivalent stoichiometric quantity of hydrogen in the solution. Here, the electrons flow from the first electrode (23) via the current conduction system (27,28) and the external load resistor (29) to the second electrode (24).

When ~~use is made of a~~ an anion-generating gas type is used, ~~such as~~ i.e. oxygen, anions are formed at the phase boundary (23.1) (gas/liquid/solid) of the first electrode (23) as a result of cathodic reduction with the stoichiometric consumption of oxygen and vapour from the gas channel (25). These anions migrate

transversely ~~to~~ through the solution flowing ~~through~~ in the ion-conducting liquid gap (32) to the second electrode (24) and at its phase boundary (24.1) (gas/liquid/solid) increases the concentration of the solution flowing in the liquid channel (26) as a result of anodic oxidation, with the ~~liberation~~ recovery of an equivalent stoichiometric quantity of oxygen in the solution. Here, the electrons flow from second electrode (24) via the current conduction system (27,28), and the external load resistor (29) to the first electrode (23).

The same state points (ZP1 to ZP4) as in Fig. 1 are assigned to the fluid flows fed to and carried off from the reaction cell. The substance potential difference of the reaction process inside the liquid gap cell arises with their assignment and hence the inherent voltage of the reaction cell. For this, the vapour-saturated gas flow is also conveyed, with transverse removal by suction of a partial quantity, preferably in the opposite direction to the solution flow and parallel to the electrode faces through the cell.

The state points (ZP1 to ZP4) of the fluid flows are set in the external part of the substance circuit. Fig. 3 shows for example in two schematic state diagrams corresponding to one another the cyclic process carried out isobarically with an aqueous ammonia solution. The carrier gas, as the third component, only makes itself felt here via the overall system pressure (P_T), and ~~this~~ is constant in the cyclic process. The saturation temperatures and saturation pressures of the vapour component and the solution are plotted in each case over the solution concentration ξ_s. Similar cyclic processes can also be carried out and presented with aqueous solutions, which form water vapour as the vapour component, whereby the solutions are diluted in the galvanosorptive reaction process.

The cyclic process according to Fig. 3 contains the following changes of state: an ~~quasi~~ isothermal ~~separa~~decomposition of the solution (input ZP4S, ZP-V→ output ZP1S, ZP4V), with the addition of heat, a substance-constant, internal, recuperative heat recirculation (input ZP1S→output ZP2'S)/(input ZP3S→ output ZP4S), a substance-constant temperature drop (input ZP2'S→ output ZP2S)$_p$ with heat emission and an ~~quasi~~ approximately isothermal, galvanosorptive reformation of the initial solution (input ZP4V, ZP2S → output ZP3S, ZP1V) with work being released to the exterior. The vapor component enriching of the solution inside the reaction cell ($\xi2\text{->}\xi3$) is equal to the vapor component depleting of the solution outside of the cell ($\xi4\text{->}\xi1$). Normally depleting/enriching rates ($\Delta\xi$s) of the solution vary from 5% to 50% change of the vapor content. The cyclic process according to Fig. 3 forms the basis for the process engineering development of the external substance circuit part, as it is represented in Fig. 4 and described below. This development of the external substance circuit part can be applied to any thermally separable solutions in combination with a carrier gas.

The heated gas vap~~ou~~r enricher (42) that is combined with a first phase separator, the solution recuperator (43), the solution cooler (44), the second phase separator (45), the solution pump (46) and the gas compressor (47) are assigned to the reaction cell (40) with external load resistor (41). The routing of the substance in the circuit is as follows:

The vapor-enriched two-phase mixture ~~[S]r, [G,V]p~~, [S,G,V]3$\mathbf{p}$ (ZP3) carried off from the liquid channel of the reaction cell (40) is fed ~~above the bottom~~ to the second phase separator (45) above its bottom and is ~~therein~~ separated into the phases [S]3$\mathbf{r}$, ~~(ZP3)~~ and [G,V]3$\mathbf{p}$. ~~(ZP3)~~. The moderately vap~~ou~~r-enriched

~~depleted~~ gas [G,V]3~~p~~, (ZP3) carried off at the head of the second phase separator (45) is united with the ~~moderately~~ vapour-depleted gas [G,V]1~~m~~, (ZP1) carried off from the gas channel of the reaction cell (40), the mixture [G,V]x, (ZP-) is fed by the gas compressor (47) to the gas vapour enricher (42) combined with the first phase separator above the bottom and is ~~in the latter~~ conveyed while taking up vapor towards the heated vapour-depleting solution [S].~~r, (ZP4).with vapour uptake.~~ The vapour-enriched gas [G,V]4~~r~~, (ZP4) carried off at the head of the gas vapour enricher (42) is fed again to the gas channel of the reaction cell (40).

The vapour-enriched solution [S]3~~r~~, (ZP3) carried off at the bottom from the second phase separator (45) is conveyed by the solution pump (46) through the secondary side of the solution recuperator (43), heating up to (ZP4) and introduced at the head into the gas vapour enricher combined with the first phase separator (42), (ZP4). The vapour-depleted solution [S]1~~p~~, (ZP1) is carried off at the bottom of the gas vapour enricher (42), ~~passing~~ed through the primary side of the solution recuperator (43), (ZP2') and through the solution cooler (44), (ZP2) and likewise fed to the liquid channel of the reaction cell (40). The substance supply and extraction of the galvanosorptive reaction cell is thus secured via the external part of the substance circuit with the retention of the substance potential difference.

On the process engineering components (40 to 47) of the external substance circuit part, the ~~ringed~~ circled state points (ZP1) ~~to~~ through (ZP4) are specified in ~~indicated according to~~ Fig. 3 ~~in~~ for each case at the substance entry and at the substance exit of the components for each individual substance flow marked with its composition [-]. They denote the changes of state of the respective substance flow inside the components (40 to 47).

Intermediate states in the substance circuit ~~, such as that at~~ on the primary-side solution exit (ZP2') of the solution recuperator (43) and ~~that~~ of the mixed flow in the gas circuit (ZP-) have also been marked. They ~~have~~ hardly have any influence on the operational properties of the galvanosorptive reaction cell.

Heat is fed from the exterior to the gas vapour enricher (42) in order to deplete ~~vaporise~~ the enriched solution [S]r from ξS4 to ξS1 by vaporising.~~, and in~~ In the solution cooler (44) only so much heat ~~there~~ is extracted from the depleted solution [S]p from T2' to T2 by cooling at the lower temperature level, ~~only so much heat~~ that the reaction process inside the galvanosorptive reaction cell (40) takes place adiabatically. The useful electrical work is extracted from the reaction cell (40) via the external load resistor (41). The drive powers of the solution pump (46) and the gas compressor (47) are small, since both conveying devices only have to ~~must convey almost without differential pressure and~~ replace ~~only~~ the flow pressure losses of the complete substance circuit and are conveying with almost no differential pressure. In the process engineering structure, the external substance circuit is independent of the design of the galvanosorptive reaction cell (Fig. 1 and Fig. 2).

A vapour purification by means of partial backflow condensation to be connected downstream of the gas vapour enricher (42) can be added for the case where, with the thermal separation of solutions with inherent vapour pressure of the solvent, too high a solvent vapour portion is contained in the vapour-saturated carrier gas and the latter, despite its continuous removal from the reaction cell, would hinder the galvanosorptive reaction process inside the reaction cell. The partial backflow

condensation can also be carried out recuperatively by using the surplus cooling potential of the vapour-enriched solution [S]r.

A cyclic process for thermo-galvanic energy conversion of a special kind is represented in Fig. 5. It becomes possible with external, electrostatic support of the galvanosorptive reaction process. In the two corresponding state diagrams (Fig. 5), in which the saturation temperatures (TV,TS) and the saturation pressures (PV,PS) of solution and vapour component are ~~each~~ plotted over the solution concentration ξS, a triangular process for each case is presented. ~~this is presented in each case as a triangular process~~. The carrier gas again makes itself felt only via the constant overall system pressure (P$_T$) of the substance circulation, whereby P$_{TOTAL}$ = P$_{VAPOR}$ + P$_{GAS}$.

The cyclic process contains ~~as~~ changes of state: an ~~quasi~~ isothermal, thermal ~~separation~~ decomposition of the solution (input ZP3S, ZP1V→output ZP3V, ZP1S), a substance-constant heating of the solution (input ZP2S→ output ZP3S) with the addition of heat from the outside, and a (polytropic) galvano-sorptive solution reformation (input ZP1S, ZP3V→ output ZP2S, ZP1V) resulting from a superimposition of isothermal substance change and isentropic, substance-constant temperature drop with work being released to the outside.

The state points are again equilibrium states for the concerning fluid flows ~~concerned~~ and are defined by their state magnitudes (P,T,ξS,ξV). The substance potential difference of the polytropic, galvanosorptive reaction process is achieved with the local assignment of the fluid flows on the reaction cell. With the additional, electrostatic support of the electrode potential, the cooling of the vapour-absorbing solution is forced with an increase of the cell working voltage. The

polytropic sorption process inside the reaction cell can be
~~conducted~~ guided in this case adiabatically or non-adiabatically
and influenced from outside by the voltage difference conferred
electro-statically on the electrodes.

The inherent cell voltage resulting from the substance potential
difference of the galvanosorptive reaction cell induces the ion
flow and hence the electron flow in the external electrical
circuit, whilst the electrostatic voltage superimposed on the
inherent voltage gives rise to the temperature drop of the
vapour-saturated solution. The additional voltage conferred
electro-statically from outside is in the polytropic sorption
process proportional to the temperature drop of the solution and
inversely proportional to the increase in concentration of the
solution. It can amount to several times the inherent voltage
value of the cell. Via the working voltage of the reaction cell,
its useful electrical work yield increases in proportional to
the electrostatic additional voltage. The starting and operating
condition for the performance of the polytropic galvanosorptive
reaction process is the presence of the inherent voltage of the
reaction cell resulting from the substance potential difference.

The cyclic process according to Fig. 5 forms the basis for the
process engineering development of the external substance
circuit part for making available the substance supply and
substance extraction of the reaction cell not in equilibrium.
The closed substance circuit is represented in Fig. 6 and is
described below. The heated solution heater (51), the gas vapour
enricher (52) combined with a first phase separator, the second
phase separator (53), the solution pump (54) and the gas
compressor (55) are assigned to the reaction cell (50) with
external load resistor (56) and are connected with the
electrostatic activation source (57). The general routing of the

substance in the external circuit part applying to such ternary substance systems is as follows:

The two-phase mixture ~~[S]r, [G,V]p,~~ [S,G,V]2, (ZP2) carried off from the liquid channel of the reaction cell (50) is fed ~~above the bottom~~ to the second phase separator (53) above the bottom and is ~~therein~~ separated into the phases [S]2r and [G,V]2, (ZP2). The vapour-depleted gas [G,V]2p, ~~(ZP2)~~ carried off at the head of the second phase separator (53) is united with the moderately vapour-depleted gas [G,V]1m, (ZP1) carried off from the gas channel of the reaction cell (50) and the mixture [G,V]x, (ZP-) is fed by the gas compressor (55) to the gas vapour enricher combined with the first phase separator (52) at the bottom and is conveyed with taking up vapor towards the heated vapour-depleting solution [S]3r, (ZP3). ~~with vapour uptake.~~ The vapour-enriched gas [G,V]3r, (ZP3) carried off at the head of the gas vapour enricher combined with the first phase separator (52) is fed again to the gas channel of the reaction cell (50).

The vapour-enriched solution [S]2r, (ZP2) carried off at the bottom of the second phase separator (53) is conveyed (ZP3) by the solution pump (54) through the solution heater (51), heated up to (ZP3), ~~and~~ introduced at the head into the gas vapour enricher combined with the first phase separator (52), and the vapour-depleted solution [S]1p, (ZP1) carried off at the bottom of the gas vapour enricher combined with the first phase separator (52) is also fed again to the liquid channel of the reaction cell (50). The substance supply and extraction of the galvanosorptive reaction cell is thus secured via the external part of the substance circuit. The individual fluid flows of the substance circuit of Fig. 6 are given as an example for the ternary substance system hydrogen as carrier gas in combination with an aqueous ammonia solution.

With extremely small vapor component-enriching and vapor component-depleting in the solution circulation ~~increases in the concentration of the solution~~ ($\Delta\xi S < 10\%$) it needs to be taken into account that the inherent voltage of the cell resulting from the substance potential difference and required for the induction of the ion flow will also be very small. In this case, the vapour-depleted solution [S]p to be fed to the reaction cell can be partially pre-cooled in a recuperator, to be provided, in the counter flow to the cooled, vapour-enriched solution [S]r and in this way the substance potential difference and thus the inherent voltage of the reaction cell can be raised.

An additional cleaning of the vapour component by means of partial backflow condensation can be added. ~~in case of need~~. The process engineering development of the substance circuit according to Fig. 6 is also applicable to any substance systems.

The assignment of the electrostatic activation source (62) to the electrical circuit of the galvanosorptive reaction cell (60) with polytropic reaction process is shown in Fig. 7 in an electrical equivalent circuit diagram. The activation source (62) is connected electrically parallel to the reaction cell (60) and to the consumer resistor (61). The activation source (62) consists of a variably adjustable direct current voltage source (63) and two blocking diodes (64,65) limiting the current flow to a few mA. The directions of the potentials of the reaction cell (60) and the activation source (62) are the same, just as the internal resistor (66) of the reaction cell (60) and the consumer resistor (61) are of the same resistance, whereby the consumer resistor (61) can be adapted to the internal resistor (66) of the reaction cell (60).

If the activation source (62) is switched off, the reaction cell (60) generates its low inherent voltage $\Delta U_{st.}$ on the basis of its

substance potential difference and the working current Iz flows via the consumer resistor (61) back to the reaction cell (60). The working voltage amounts here to $\Delta U_{eff.} = \Delta U_{st.} - I_{eff.} \times R_z$. When the activation source (62) is switched on, the voltage ΔU_o increases to the electrostatic voltage ΔU_{est}, while the working current portion $I_{eff.} = I_z + \frac{1}{2}ID$ is flowings via the consumer resistor (61), ~~at the voltage $\Delta U_o = \Delta U_{st.} + \Delta U_{est.}$ increased by the electrostatic voltage portion $U_{est.}$, whilst~~ the ~~cell~~ working current portion $(I_z - \frac{1}{2}ID)$ is flowings back to the reaction cell (60) and the conducting-state current ID cominges from the activation source (62) is ~~and~~ flowings back to it again. The working voltage of the reaction cell (60) amounts here to $\Delta U_{eff.} = \Delta U_{est.} - (I_z - \frac{1}{2}ID) \times R_z$, whereby the conducting-state current ID (≤ 10 mA) is very much smaller than the inherent cell current Iz (≥ 500 mA) and thus ~~negligible~~ insignificant in comparison to the inherent reaction cell current. The electrostatic voltage $\Delta U_{est.}$, resulting from the solution cooling of the polytropic reaction process, increases the electrical power of the reaction cell (60). ~~increased by the electrostatic voltage portion $U_{est.}$ results from the solution cooling of the polytropic reaction process.~~

Abstract

The invention relates to a galvanosorptive reaction cell with closed substance circulation for the conversion of low temperature heat, preferably of waste heat into useful electrical work. The reaction cell and the accompanying isobaric substance circuit are presented. The galvanosorptive reaction process inside the cell is carried out polytropically with an electrostatic auxiliary voltage, which is superimposed onto the inherent voltage of the cell. ~~In this way~~ Therefore, not only free reaction work can be extracted from the reaction system, but, ~~with cooling of the reaction system,~~ by cooling of the reaction system also substance-bound reaction work.~~, can be extracted from the reaction system.~~ The electrical energy yield and the power density of galvanosorptive reaction cell are thereby increased many times over.

Fig. 1

$$ZP\ (1):\quad \begin{array}{l} S_I \\ S_{II} \end{array} \quad \begin{array}{l} |NH_3^v, H_2^g| \\ \hline |H_2O^v, O_2^g| \end{array} \qquad [P^v, P^g, T, \xi^v]$$

$$ZP\ (2):\quad \begin{array}{l} S_I \\ S_{II} \end{array} \quad \begin{array}{l} |NH_3^{aq}| \\ \hline |LiBr^{aq}| \end{array} \qquad [P^{aq}, T, \xi^{aq}]$$

$$ZP\ (3):\quad \begin{array}{l} S_I \\ S_{II} \end{array} \quad \begin{array}{l} |NH_3^{aq}, NH_3^v, H_2^g| \\ \hline |LiBr^{aq}, O_2^g, H_2O^v| \end{array} \qquad [P^{aq}, P^v, P^g, T, \xi^{aq}, \xi^v]$$

$$ZP\ (4):\quad \begin{array}{l} S_I \\ S_{II} \end{array} \quad \begin{array}{l} |NH_3^{vi}, H_2^g| \\ \hline |H_2O^v, O_2^g| \end{array} \qquad [P^v, P^g, T, \xi^v]$$

Fig. 2

$$S_{III} \quad |H_2O^v, H_2{}^g| \; H_3O^+, \; EL \; |H_2SO_4{}^{aq}, H_2{}^g|$$

$$S_{IV} \quad |H_2O^v, O_2{}^g| \; OH^-, \; EL \; |H_2SO_4{}^{aq}, O_2{}^g|$$
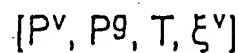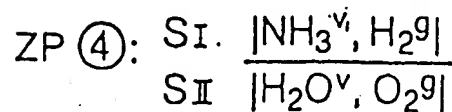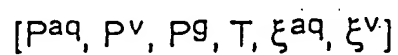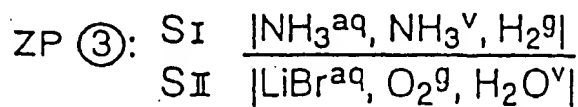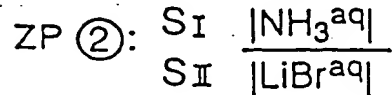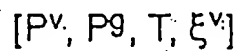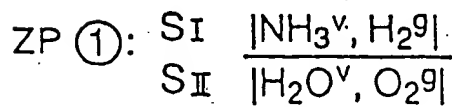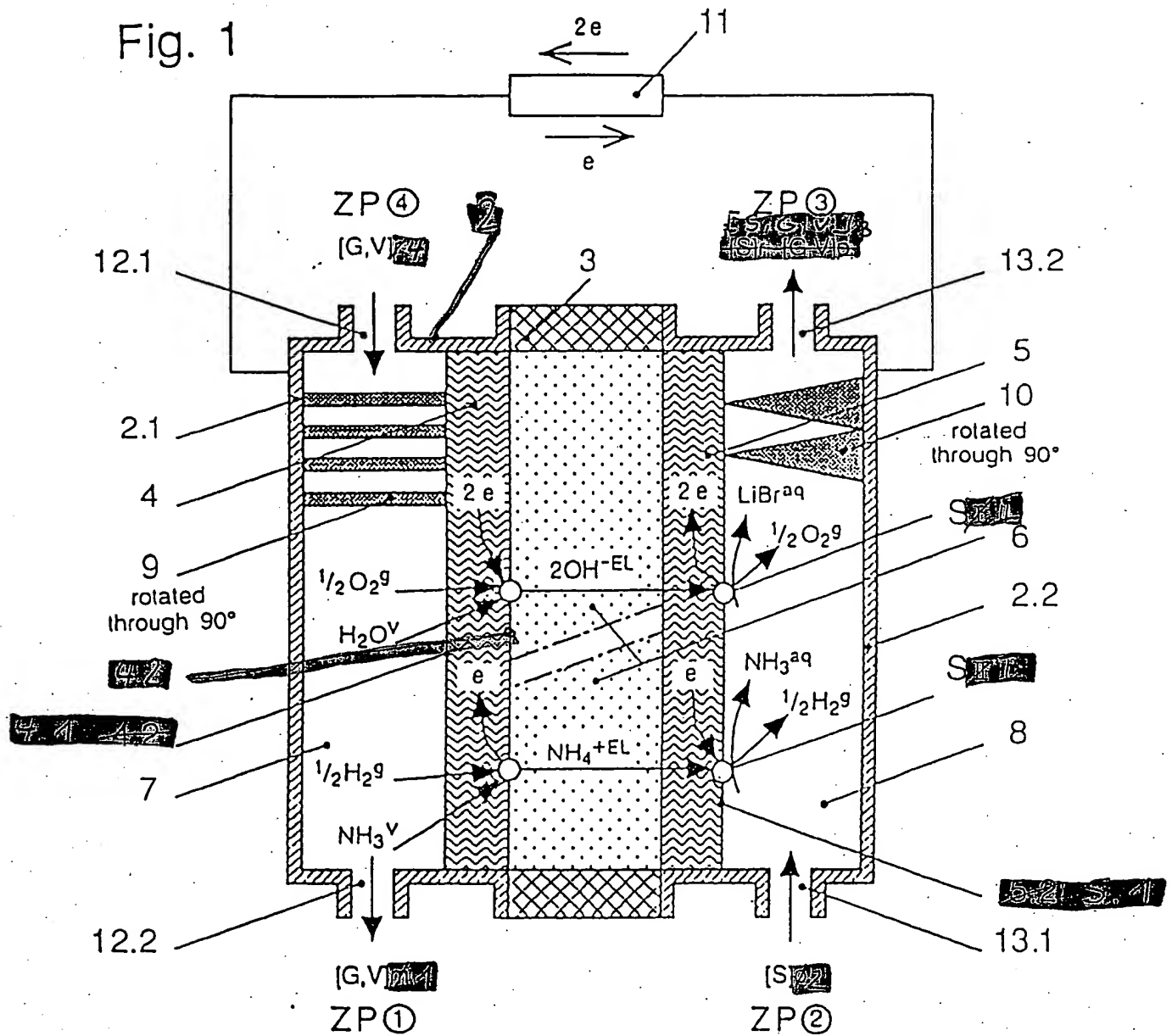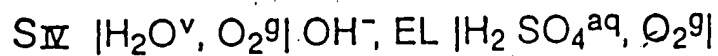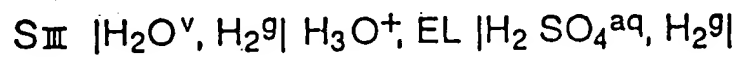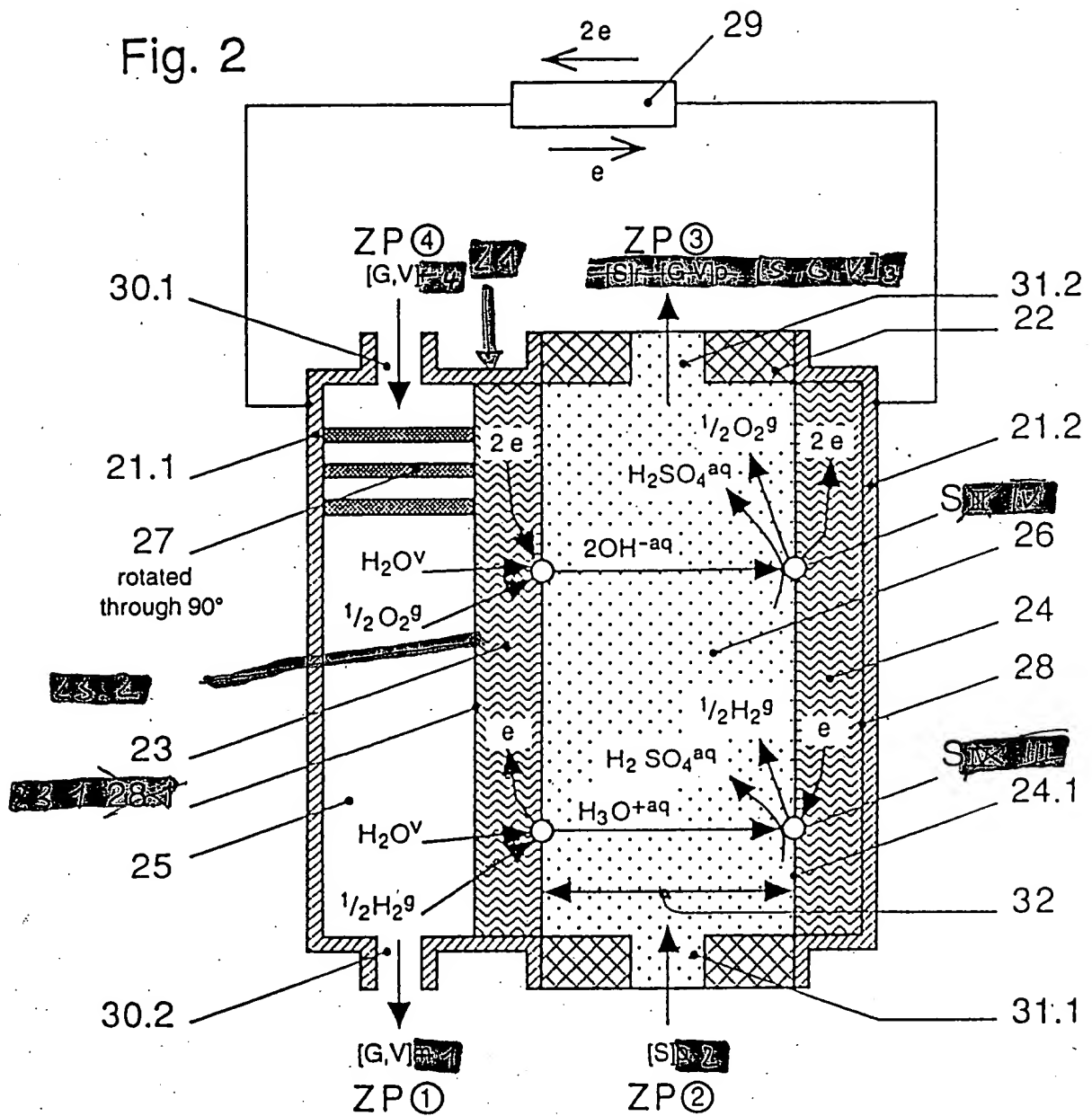
State points (ZP) in accordance with Fig. 3

Fig. 3

Fig. 4

Heat Input

Heat output

Useful work output

G: Gas
V: Vapour
S: Solution

Fig. 5

Fig. 6

G: Gas
V: Vapour
S: Solution

Heat input

Useful work output

Fig. 7

$\Delta U_{est.}$

I_D

I_D

62

65 63 64

Ra

60

66

Rz

$I_z - \frac{1}{2} I_D$

$\Delta U_o = \Delta U_{st} \cdot \Delta U_{est.}$

$I_{eff} = I_z + \frac{1}{2} I_D$

Rv

61